# Application of Response Surface Methodology in Optimization of Cadmium Adsorption By Raw Rice Husk

Monik Kasman
Civil and Environmental Engineering dept
Engineering Fac. University of Malaya
Environmental Engineering Dept, Engineering Faculty,
University of Batanghari,
Jambi, Indonesia
E-mail: emka_engineer@yahoo.com

Shaliza Ibrahim
Civil and Environmental Engineering department
Engineering Faculty, University of Malaya
Kuala Lumpur Malaysia
E-mail: shaliza@um.edu.my

***Abstract*** **— this study was aimed to model and optimize the adsorption process of cadmium from aqueous solution onto raw rice husk (RRH). The batch experiment was carried out in four factors as a function of pH (A: 5 – 9), adsorbent dosage (B: 2 – 8 g/100 ml), contact time (C: 60 – 240 minutes) and initial concentration of adsorbate (D: 70 – 110 mg/L) to response (percentage of cadmium removal). Response surface methodology (RSM) was used to analyzed and optimize the effect of four factors in cadmium adsorption. The result showed that RRH can successfully reduce cadmium from aqueous solution in removal percentage from 79.45% to 97.978%. Value of pH, dosage, contact time and initial concentration was noted significant statistically. RSM was undoubtedly used to optimize the adsorption process where the optimum condition achieved at pH 9, dosage 5 g/100 ml, contact time 240 minutes and initial cadmium concentration 90 mg/L.**

*Keywords- Adsorption; Cadmium; Response surface methodology; Raw rice husk*

## I. INTRODUCTION

Water and wastewater containing heavy metals has been concerned environmental crisis in worldwide due to the harmful impact. Some of the heavy metals are essential in trace amounts by living organism, but, the excess of a threshold concentration will be dangerous toxic to living organism as well as environment. As highly toxic metal, cadmium which is derived from commonly of anthropogenic activities such as phosphate fertilizer, fossil fuel combustion and industrial activities produces adverse health effects on human being. The accumulation of cadmium in human body causes high blood-pressures, liver disease, nerve or brain damage, even cancer [1], [4]. Clearly, it was needed the innovative treatment to reduce cadmium concentration attaining permitted toxicity threshold level.

Development of easy and economical technique of heavy metals treatment including cadmium is definitely a priority in recent years. Some of them are electro-coagulation, reduction and precipitation, ion exchange and reverse osmosis [3]. However, most of these methods suffer from drawbacks like high capital and operational cost and problems in disposal of the residual metal sludge [10]. Adsorption has been recommended as alternative attractive treatment for few years. It employs some adsorbents from industrial, agricultural and biomass waste. Some previous researches have done adsorption in reducing of cadmium in wastewater [1]-[3], [5]-[8], [10], but only a few of them focusing on optimization of cadmium using rice husk by certain statistical tools.

Rice husk, a by-product of the rice milling industry, was favorable selected as an adsorbent in several wastewater treatment by reason of its local availability, low production cost, insolubility in water, granular structure, high mechanical strength, and chemical stability [10], [11]. As previous researches proved that rice husk, either treated or untreated was effective on heavy metal removal [1], [5], [6], [10], [11].

Response surface methodology (RSM) is a collection of mathematical and statistical approach for experimental design useful for analyzing and evaluating the effects of variable as well as searching optimum conditions of variable to predict targeted responses [2], [7]. RSM has been proven to be successfully implemented in some researches, such as engineering, food processing, biotechnology and adsorption processes for optimization [2], [3], [7], and [8].

The main purposes of this study are to model and to optimize adsorption of cadmium using raw rice husk (RRH) by RSM under DESIGN EXPERT software. Besides, investigation to the effect of pH, adsorbent dosage, contact time and initial concentration also was done.

## II. MATERIALS AND METHODS

### A. Adsorbent

Rice husk were obtained from a nearby rice mill in Kuala Selangor. Rice husk was washed for 2 – 4 times with tap water continued with distilled water to remove all dirt particles and impurities. The washing process was stopped until no color in the washed water. Next, for preparing RRH, the washed rice husk was dried at 100$^o$C to get rid of moisture and impurities until the weight of rice husk become constant. Then it was ground with food processor (national MK 110) and sieved to a particle size of ≤ 600 µm. Finally, the adsorbent was stored in air-tight container at room temperature until testing.

### *B. Batch study*

Stock solution of cadmium (1000 mg/L) was prepared by dissolving 2.75 g cadmium nitrate ($Cd(NO_3)_2.4H_2O$) in distilled water, and certain concentrations of cadmium were obtained by further dilutions The pH of each last solution was adjusted to the required value with diluted and concentrated $H_2SO_4$ and NaOH solution. All the chemicals used were of analytical reagent grade.

Batch experiment was carried out with variation of the four factors including pH, initial concentration of cadmium aqueous solution, adsorbent dosage and contact time as shown in Table.1. The 29 runs with all combinations of factors for each adsorbent were randomly performed according to a box-behnken statistical design (BBD), one of Response Surface Methodology experimental design under Design Expert 6.0.8 stat ease software (Stat-Ease Inc., Minneapolis, MN,USA) for linear, quadratic and interaction effects of four factors. All the experiments conducted in duplicate and mean values were presented. The removal efficiency of cadmium solution was defined as equation 1:

$$Y = \left(\frac{C_i - C_e}{C_i}\right) \ x\ 100 \qquad (1)$$

Where, $C_i$ = initial concentration (mg/L), $C_f$ = final concentration (mg/L) and m = mass of adsorbent (g/L).

## III. Results and discussion

### *A. Stastical Analysis*

As seen Table 1, performance of RRH in reducing cadmium from aqueous solution was satisfied whereas the removal up to 100%. It was also noted that these recent result have high dependence and correlation between the observed values and predicted values of responses due to value of $R^2$ and adjusted $R^2$ over raw rice husk is more than 80% or in other word regression model provides an excellent explanation of the relationship between the independent variables (pH, adsorbent dosage, contact time, initial concentration) and the response (cadmium removal) (Table 4.2). The Pred R-Squared of RRH obtained 0.994 is in reasonable agreement with the Adj R-Squared of RRH (0.986).

Table 2 is presented the analysis of variance producing by the statistical analysis using the DESIGN EXPERT 6.0.8 software. Previously mentioned that the significant factor and interaction between factors are noticed

TABLE I. DESIGN AND OBTAINED RESULTS

| No | pH (A) | Adsorbent dosage (B) | Contact time (C) | Initial concentration (D) | Cd Removal |
|---|---|---|---|---|---|
| | | g/100 ml | minutes | mg/L | % |
| 1 | 7 | 5 | 60 | 110 | 56.318 |
| 2 | 7 | 5 | 150 | 90 | 72.789 |
| 3 | 7 | 5 | 150 | 90 | 69.444 |
| 4 | 9 | 8 | 150 | 90 | 91.573 |
| 5 | 7 | 8 | 150 | 110 | 72.123 |
| 6 | 7 | 2 | 150 | 70 | 55.636 |
| 7 | 7 | 5 | 150 | 90 | 73.6 |
| 8 | 7 | 5 | 240 | 70 | 77.514 |
| 9 | 7 | 2 | 150 | 110 | 40.673 |
| 10 | 5 | 2 | 150 | 90 | 45 |
| 11 | 9 | 2 | 150 | 90 | 94.837 |
| 12 | 7 | 8 | 60 | 90 | 68.083 |
| 13 | 5 | 5 | 240 | 90 | 72.278 |
| 14 | 5 | 5 | 150 | 70 | 65.657 |
| 15 | 5 | 5 | 150 | 110 | 56.35 |
| 16 | 7 | 5 | 150 | 90 | 70.389 |
| 17 | 7 | 8 | 240 | 90 | 81.772 |
| 18 | 7 | 2 | 60 | 90 | 43.761 |
| 19 | 7 | 5 | 150 | 90 | 71.856 |
| 20 | 9 | 5 | 150 | 110 | 92.925 |
| 21 | 9 | 5 | 240 | 90 | 95.221 |
| 22 | 7 | 2 | 240 | 90 | 67.35 |
| 23 | 7 | 8 | 150 | 70 | 77.757 |
| 24 | 7 | 5 | 60 | 70 | 65.286 |
| 25 | 5 | 5 | 60 | 90 | 53.911 |
| 26 | 5 | 8 | 150 | 90 | 64.028 |
| 27 | 7 | 5 | 240 | 110 | 73.286 |
| 28 | 9 | 5 | 60 | 90 | 92.625 |
| 29 | 9 | 5 | 150 | 70 | 89.684 |

with the the p-value less than 5% (< 0.05). The summary output of ANOVA of RRH-Cd removal in Table 2 shows that the Rcubic model was significant due to the p-value <0.0001, and all of factors was significantly influenced to the response. Actually, the adsorption process of cadmium was also manipulated by interaction of some factors as shown in Table 2 (coded) including AB, AC, AD, BC and BD. The model can be developed due to the P-value of the lack of fit (LOF) attained for this model was valid (0.4372) for the present work. All of insignificant model terms having limited influence were excluded to improve the model. The construction equation for this model is stated in equation (2).

$$\text{RRH-Cd removal} = 71.323+15.282*A+13.393*B + 8.309*C -2.408*D+7.970*A^2-5.967*B2-3.390*D^2- 5.573*A*B-3.943*A*C+3.137*A*D- 2.475*B*C + 2.332*B*D - 9.452*A^2*B - 3.069*A^2*C + 4.064*A*B^2-2.742*B^2*D - 3.707*B*C^2 \quad (2)$$

This validity of this equation model was also supported by the Figure 1 and Figure 2 which illustrated statistically that residual point followed the normal distribution and the residual run was scattered in the outlier T

TABLE 2. ANALYSIS OF VARIANCE

| Source | Coef | SS | F | P |
|---|---|---|---|---|
| Model | 71.323 | 6490.031 | 113.47 | < 0.0001 |
| A | 15.282 | 1868.366 | 555.32 | < 0.0001 |
| B | 13.393 | 717.474 | 213.25 | < 0.0001 |
| C | 8.309 | 552.358 | 164.17 | < 0.0001 |
| D | -2.408 | 46.376 | 13.784 | 0.0034 |
| A2 | 7.97 | 427.306 | 127.01 | < 0.0001 |
| B2 | -5.967 | 239.524 | 71.192 | < 0.0001 |
| D2 | -3.39 | 77.317 | 22.98 | 0.0006 |
| AB | -5.573 | 124.23 | 36.924 | < 0.0001 |
| AC | -3.943 | 62.182 | 18.482 | 0.0013 |
| AD | 3.137 | 39.364 | 11.7 | 0.0057 |
| BC | -2.475 | 24.503 | 7.283 | 0.0207 |
| BD | 2.332 | 21.756 | 6.466 | 0.0273 |
| A2B | -9.452 | 178.676 | 53.107 | < 0.0001 |
| A2C | -3.069 | 25.113 | 7.464 | 0.0195 |
| AB2 | 4.063 | 44.032 | 13.087 | 0.004 |
| B2D | -2.742 | 20.044 | 5.958 | 0.0328 |
| BC2 | -3.707 | 27.48 | 8.168 | 0.0156 |
| Residual | | 37.009 | | |
| Lack of Fit | | 25.418 | 1.253 | 0.4372 |
| Pure Error | | 11.591 | | |
| Cor Total | | 6527.04 | | |

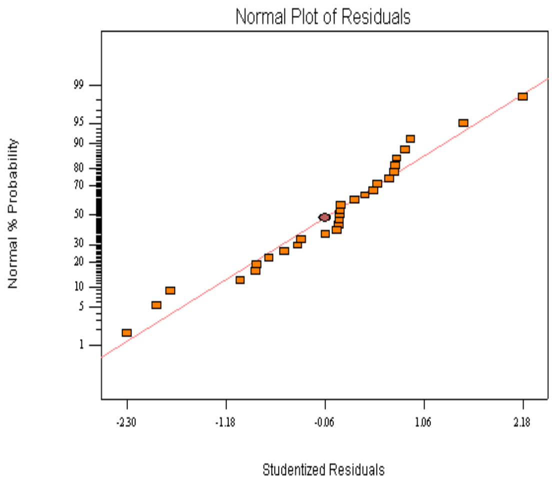


Figure 1. Diagnostic Plot-Normal Probability of The chosen model

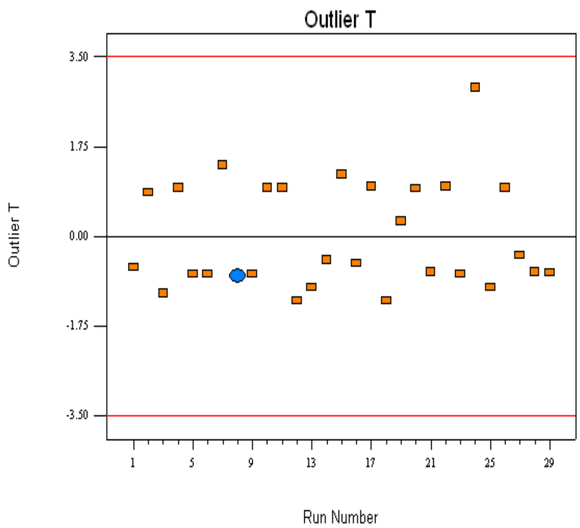


Figure 2. Diagnostic Plot-Outlier T of The chosen model

## *B. Effects of factors to cadmium removal*

Normally, all of graphs in Figure. 1 illustrates that the increase of removal occurring in the increase of pH of alkali, the increase of adsorbent dosage, the decrease of initial concentration and the increase of contact time. Furthermore, those graphs also point out that the interaction between of factors over response was very significant influencing the cadmium adsorption process using RRH. These were contact time over pH and over initial concentration.

The plots view of response surface (Figure 3a–d) visualized the cadmium removal using RRH over different combinations of factors. It was corresponded to a function of two factors at a time, occupying other factors at a fixed level [2].

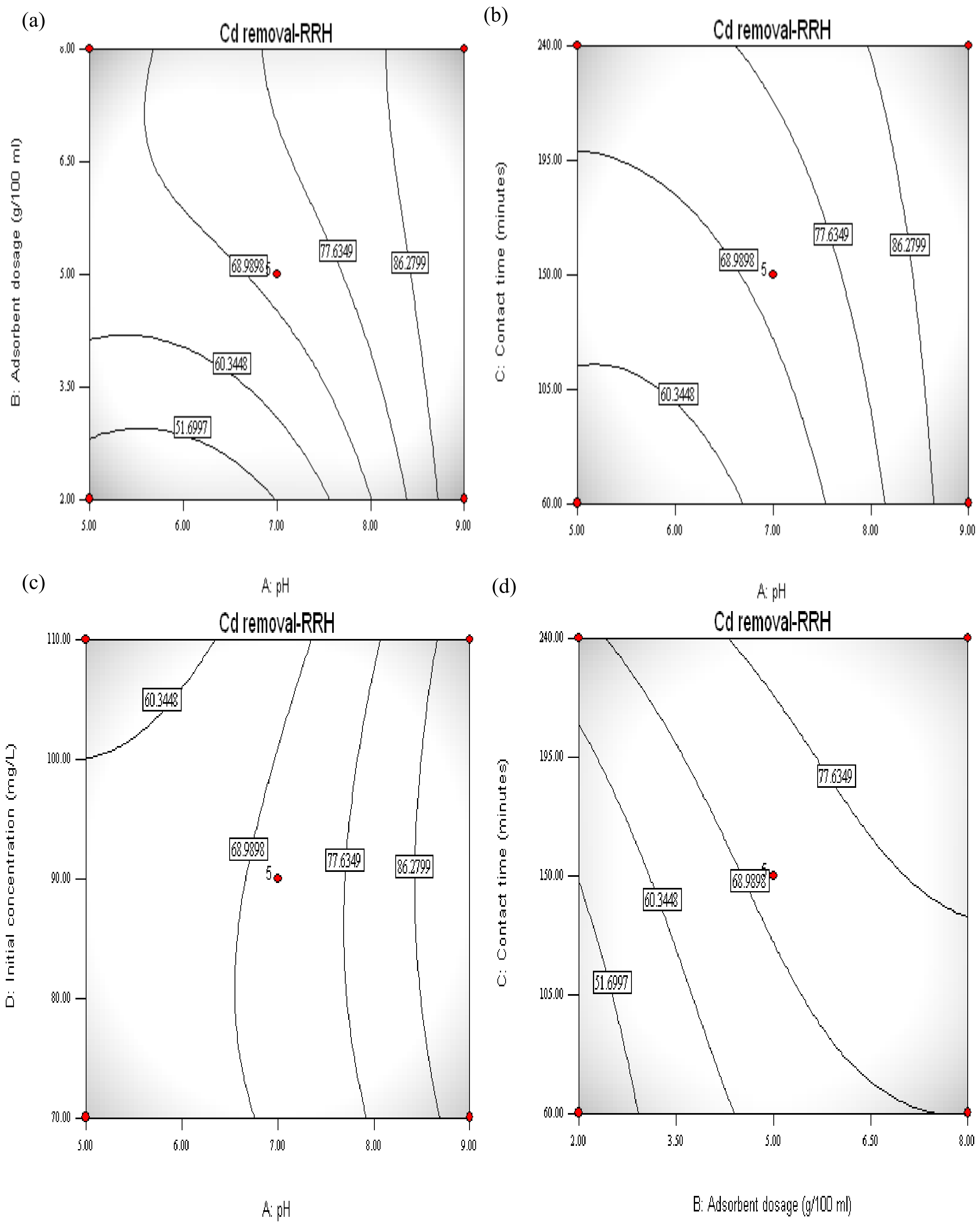


Figure 3. The contour plot for the effect of (a) pH and adsorbent dosage; (b) pH and contact time; (c) pH and initial concentration; (d) adsorbent dosage and contact time

According to Figure 3, the response surface plots pointed out that RRH successfully reduced cadmium concentration from aqueous solution. All of factors were significant in reducing of adsorption that either indicated in P-value (less than 5%) or reflected in the plot of response surface. The plot was also used to determine adsorption of the cadmium concentration (mg/L) for combinations of interactive factors like pH, adsorbent dosage, contact time initial cadmium) concentration. The curved contour lines and table ANOVA shown that there was a significant interaction between pH and dosage, pH and contact time, pH and initial concentration, dosage and contact time as well as dosage ad initial concentration.

Figure 3 (a–d) shows the interaction between pH to three other factors (adsorbent dosage, contact time and initial concentration. Value of pH and contact time was highly significant in adsorption process as reflected their P-values. Clearly, appropriate pH for process was in neutral or alkali condition (more than 7). The reason for this condition was probably due to the presence of a large number of $H^+$ ions, which in turn neutralize the negatively charged adsorbent surface thereby reducing hindrance to the diffusion of iron [3]. Further, Deepak and Gupta, 1991 was quoted by Bishnoi et al and Kiran et al stated that the effect of pH is also governed by the development of an electrical double layer on the surface adsorbent. The surface of adsorbent were more negative, caused the change in polarity from positive to negative as the $H^+$ changes from acidic to basic region. This accounts for the downfall in the adsorption of iron at increased pH [4] [5].

Adsorbent dosage, contact time and initial concentration also have significant factors in cadmium removal as marked from the equation and plot (Figure 3). As a result of increasing in contact time and decreasing in initial concentration, the cadmium removal increased. Some previous researches reported similar condition whereas the higher adsorbent dosage, the higher adsorption removal [1], [3], [5]-[8], [10]. This phenomenon was due to enhance of adsorbent surface availability in adsorbing of solute [10]. The less initial concentration of cadmium ensued increasing of the mass transfer driving force. Consequently, the rate of cadmium passes the bulk solution to the particle surface [1], [2].

## IV. CONCLUSSIONS

The findings obtained from current study are concluded below:

1. The Use of Response surface methodology, in batch experiment was strong useful to optimize and to model the adsorption process in purposing to get optimum condition for cadmium adsorption process using raw rice husk.
2. The obtained results indicated that the cadmium removal by RRH reached up to 100%, of which was in range 40.673% – 95.221%.
3. The Cadmium adsorption process using RRH was noted dominated significantly by all of factors (pH, adsorbent dosage, contact time and initial concentration).

## ACKNOWLEDGMENT

Authors are grateful to IPPP (Institute of Research Management and Monitoring) of University of Malaya for financial support

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